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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 7/29/92		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Detection of CH_3 During CVD Growth of Diamond by Optical Absorption				5. FUNDING NUMBERS DAAL03-90-6-0115	
6. AUTHOR(S) M. A. Childs, K. L. Menningen, P. Chevako, N. W. Spellmeyer, L. W. Anderson, J. E. Lawler				8. PERFORMING ORGANIZATION REPORT NUMBER Phys. Lett. A reprint 1	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Wisconsin 1150 University Ave. Madison, WI 53706				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211				11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The absolute concentration of CH_3 is measured during diamond growth for a range of input CH_4 concentrations using multi-element optical absorption spectroscopy at wavelengths near 216 nm. A detection limit of 2×10^{11} CH_3 radicals/ cm^3 has been achieved. We also detect C_2H_2 during diamond growth using the same technique.					
14. SUBJECT TERMS				15. NUMBER OF PAGES 3	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
				20. LIMITATION OF ABSTRACT UL	

93 5 05 120

93-09827



Detection of CH_3 during CVD growth of diamond by optical absorption

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Received 6 August 1992; revised manuscript received 17 September 1992; accepted for publication 18 September 1992
Communicated by B. Fricke

The absolute concentration of CH_3 is measured during diamond growth for a range of input CH_4 concentrations using multi-element optical absorption spectroscopy at wavelengths near 216 nm. A detection limit of 2×10^{11} CH_3 radicals/ cm^3 has been achieved. We also detect C_2H_2 during diamond growth using the same technique.

This paper reports the first application of ultra-sensitive multi-element absorption spectroscopy to the measurement of radical or molecular densities in a chemical vapor deposition (CVD) system. Diamond can be grown by CVD when a mixture CH_4 and H_2 gas is flowed past a hot filament onto a heated substrate. There is substantial evidence that the methyl radical (CH_3) is a gas phase precursor under a variety of conditions [1-4]. The acetylene molecule (C_2H_2) may also be a precursor of diamond [5,6]. It is particularly challenging to obtain reliable measurements of the absolute density of polyatomic radicals such as CH_3 . All electronically excited states of CH_3 dissociate, thus laser-induced fluorescence measurements on CH_3 are not possible. During the CVD growth of diamond we have measured the absolute concentration of CH_3 in situ by using multi-element absorption spectroscopy. We also have detected C_2H_2 by using this method. The gas phase precursor candidate CH_3 has been previously detected with REMPI [7], near-threshold ionization mass spectrometry [8], and infrared diode laser absorption spectroscopy [9]. The technique reported in this paper has great advantages over previous techniques in that it is simple, non-invasive, linear, and highly sensitive. Furthermore, this technique can yield absolute densities of a variety of other radicals or molecules in low concentrations and under many different conditions, and is generally applicable to

measurements in growth, etching, or other systems.

Diamond is grown in this experiment by using eight 0.25 mm diameter tungsten filaments mounted in parallel and heated to 2600 K. These filaments are 1.9 cm long, 1.6 cm apart, and 1.5 cm below the substrate, as shown in fig. 1. The silicon $\langle 100 \rangle$ substrate on which diamond is grown is 9.5 cm long, 1.3 cm wide, 0.5 mm thick, and is kept at 1100 K during the experiment. The substrate is prepared for diamond growth by scratching with 1 μm diamond paste followed by cleaning. The concentration of methane in the feed gas varies from 0.25% to 7% by volume in H_2 . A total pressure of 20 Torr and a total flow rate of 100 SCCM is maintained in these experi-

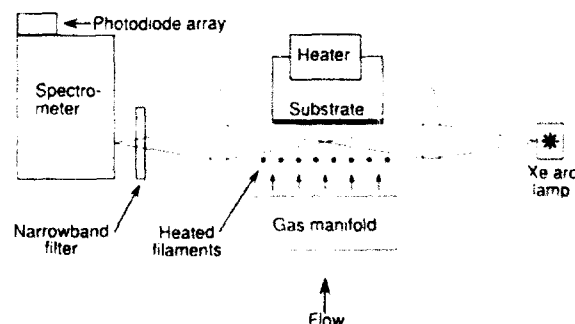


Fig. 1. Schematic diagram of the apparatus for obtaining absorption spectra. The filaments are shown in cross-section, with their length perpendicular to the page.

ments. Diamond is grown only for low CH_4 input concentrations. We verify diamond growth both by scanning electron microscopy to observe the diamond crystals on the substrate and by Raman spectroscopy to detect the 1332 cm^{-1} line characteristic of crystalline diamond.

Absorption spectroscopy is performed with an ultrastable xenon arc lamp (Optical Radiation Corp. USAN 150-7) as a continuum source. The $1\text{ mm} \times 2\text{ mm}$ arc is imaged with unity magnification at the center of the diamond growth system, 0.7 cm above the filaments, and is then reimaged with unity magnification on the entrance slits of a 0.5 m spectrometer (Spex 1870B). Schlieren grade, wedged, fused silica windows are used on the growth chamber. An interference filter centered at 200 nm and with a 25 nm bandpass (Acton Research Corp. 200-N-2D) is used before the entrance of the spectrometer to eliminate longer wavelength scattered light in the spectrometer. A photodiode array (Princeton Instruments PDA 1024) is used to detect the light at the exit focal plane of the spectrometer. The individual pixels in the photodiode array are $25\text{ }\mu\text{m}$ wide and 2 mm tall. This pixel width corresponds to a spectral limit of resolution of 0.04 nm . Since the CH_3 absorption feature is about 1.2 nm wide, the entrance slit can be opened up and neighboring pixels can be averaged together without loss of information. These actions improve the signal-to-noise ratio because the noise in our experiment is limited by photon statistics. Even in the high resolution spectra recorded by Herzberg and Shoosmith [10], the CH_3 absorption feature has no significant rotational structure, due to rapid dissociation of the CH_3 excited electronic state. At high resolution Herzberg has observed two peaks in the CH_3 absorption spectrum at wavelengths 215.8 and 216.4 nm . When we operate our system at a spectral limit of resolution of 0.12 nm these two peaks in the CH_3 spectrum are clearly observed.

The absorption data are obtained by collecting a spectrum with both methane and hydrogen flowing into the chamber. A background spectrum is then taken with only hydrogen flowing into the chamber. Each of the spectra is corrected by subtracting the dark counts, and then the corrected absorption spectrum is divided by the corrected background spectrum. A typical absorption profile is shown in fig. 2. Two main features are apparent. The first and dom-

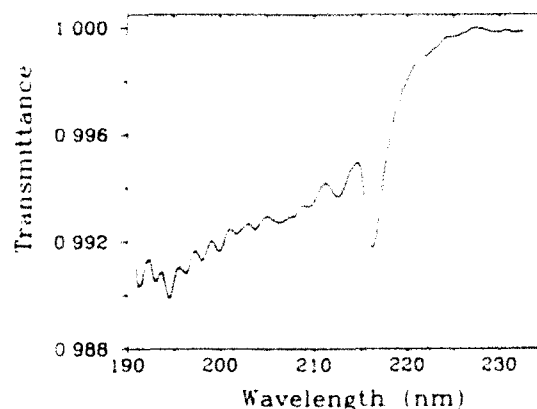


Fig. 2. Typical absorption profile for CH_3 with 2% CH_4 input concentration at a spectral limit of resolution of 0.76 nm . The oscillations in the spectrum between 190 and 206 nm are due to C_2H_2 absorption and are very repeatable.

inant feature is the CH_3 absorption at 216.4 nm . The second feature is the absorption observed at shorter wavelengths. Acetylene absorption probably accounts for much of the apparent step in the spectrum of fig. 2 at wavelengths shorter than 216 nm , and is responsible for the oscillations in the absorption spectrum between 190 and 206 nm .

The CH_3 concentration is obtained by dividing the logarithm of the transmittance at 216.4 nm by the product of the peak absorption cross section of $3.9 \times 10^{-17}\text{ cm}^2$ [11] and the effective path length of 12.7 cm . This cross section was measured at room temperature, and we have neglected the changes in the peak cross section due to changes in the temperature-dependent partition function. The largest source of uncertainty in this experiment is due to a lack of knowledge of the baseline for the absorption measurement of CH_3 . We believe this uncertainty is about $\pm 20\%$. The point to point uncertainty is much less than 20% , and represents the reproducibility of the data. The error bars shown in fig. 3 result only from the reproducibility of the data. This simple optical absorption technique is highly sensitive because of the good stability of the Xe arc lamp and because of the multi-element detector array. In contrast to a single element detector, a multi-element detector array is very sensitive because slow drifts in the lamp intensity appear in all elements simultaneously. Taking into account the signal-to-noise ratio of collected spectra, we have achieved a detection limit of 2×10^{11}

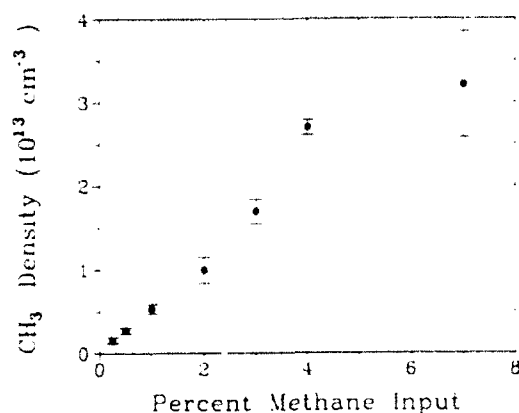


Fig. 3. Absolute CH₃ density as a function of input CH₄ concentration for $T_{\text{filament}} = 2600$ K, $T_{\text{substrate}} = 1073$ K, and 20.0 Torr total pressure.

CH₃ radicals/cm³, corresponding to a fractional absorption of 1×10^{-4} .

We observe many C₂H₂ absorption bands at wavelengths below the CH₃ absorption. We are pursuing the simultaneous measurement of CH₃ and C₂H₂ concentrations during diamond growth. The C₂H₂ bands show substantial variation with temperature. Because our system has large gas temperature gradients, modifications will be required before we can reliably determine the absolute C₂H₂ concentration.

Results from the absorption measurements of CH₃ are presented in fig. 3. The CH₃ concentration is observed to increase linearly with the CH₄ concentration in the feed gas for low CH₄ concentrations. At higher CH₄ concentrations the CH₃ density apparently starts to saturate. Very similar behavior has been observed by Hsu using near-threshold ionization mass spectrometry to detect CH₃ [12]. It is worth noting that our absorption measurements are similar to Hsu's measurements. The normalization of near-threshold ionization mass spectrometry data is a difficult problem. The absorption experiment reported here is simpler, is non-invasive, and produces more reliable absolute densities than other methods for detecting the CH₃ radical.

The CH₃ density increases monotonically with the CH₄ percentage in the feed gas, and there is evidence in fig. 3 of a saturation in the CH₃ density at CH₄ percentages above 4%. Diamond growth peaks for

CH₄ percentages near 1% and ceases for CH₄ percentages above ~2% [3]. The failure to grow diamond at higher CH₄ percentages may be due to depletion of atomic hydrogen [12] or due to poisoning of the filament. It is not due to a lack of methyl radicals.

A version of this experiment has been used for absorption spectroscopy in glow discharge plasmas by Wamsley et al. [13]. A digital subtraction technique has been developed to discriminate against the line emission from the glow discharge and to detect only the continuum emission from the arc. The continuum emission has absorption features after traversing the glow discharge. Wamsley et al. studied an intense 400 mA glow discharge, and we expect this technique will work well on glow discharges used for diamond deposition.

Funding for this work is provided by the Army Research Office, Grant DAAL03-90-G-0115. K.L.M. is supported by a graduate fellowship from the Office of Naval Research.

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